

What is claimed is:

1. An energy curable composition comprising:

an at least difunctional thiol compound; and

an at least difunctional ethylenically unsaturated compound;

wherein at least one of the thiol compound and the ethylenically unsaturated compound is at least partially halogenated,

the ratio of thiol moieties to ethylenically unsaturated moieties is between about 1:2 and about 2:1, and

the thiol compound and the ethylenically unsaturated compound account for between about 35% and about 99.9% by weight of the energy curable composition.

2. The energy curable composition of claim 1 further comprising a selected amount of a free radical initiator.

3. The energy curable composition of claim 1 wherein at least one of the thiol compound and the ethylenically unsaturated compound includes a perfluorinated moiety.

4. The energy curable composition of claim 1 further comprising a C_H of less than about 55 M.

5. The energy curable composition of claim 1 further comprising a C_H of less than about 35 M.

6. The energy curable composition of claim 1 further comprising a C_H of less than about 20 M.

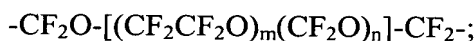
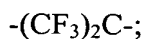
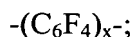
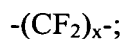
7. The energy curable composition of claim 1 further comprising a C_H of less than about 15 M.

8. The energy curable composition of claim 1 wherein the ratio of thiol moieties to ethylenically unsaturated moieties is between about 9:10 and about 10:9.

9. The energy curable composition of claim 1 wherein the ratio of thiol moieties to ethylenically unsaturated moieties is between about 19:20 and about 20:19.

10. The energy curable composition of claim 1 wherein at least one of the thiol compound and the ethylenically unsaturated compound is at least trifunctional.

11. The energy curable composition of claim 1 wherein the perfluorinated moiety is selected from the group consisting of:



wherein x is an integer between 1 and about 10;

m and n designate the number of randomly distributed perfluoroethyleneoxy and perfluoromethyleneoxy backbone repeating subunits, respectively; and p designates the number of $-\text{CF}(\text{CF}_3)\text{CF}_2\text{O}-$ backbone repeating subunits.

12. The energy curable composition of claim 11 wherein the perfluorinated moiety is $-\text{CF}_2\text{O}-[(\text{CF}_2\text{CF}_2\text{O})_m(\text{CF}_2\text{O})_n]-\text{CF}_2-$ and the ratio of m to n varies from about 0.5:1 to about 1.4:1.

13. The energy curable composition of claim 12 wherein the ratio of m to n is about 1:1 and the molecular weight of the ethylenically unsaturated compound is between about 2000 and about 2800.

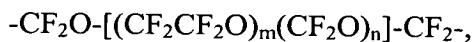
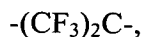
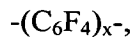
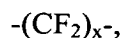
14. The energy curable composition of claim 1 wherein the ethylenically unsaturated moieties are selected from the group consisting of acrylate, methacrylate, vinyl ether, allyl ether, alkene, thioacrylate ester, thiomethacrylate ester, vinyl thioether, allyl thioether, and maleimide.

15. The energy curable composition of claim 1 wherein the ethylenically unsaturated compound has the structure



wherein

R_f is a perfluorinated moiety selected from the group consisting of:



wherein x is an integer between 1 and about 10;

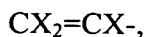
m and n designate the number of randomly distributed perfluoro-ethyleneoxy and perfluoromethyleneoxy backbone repeating

subunits, respectively; and

p designates the number of $-CF(CF_3)CF_2O-$ backbone repeating subunits;

R and R' are divalent or trivalent connecting moieties selected individually from the group consisting of alkyl, aryl, ester, ether, amide, amine, and urethane groups;

A is an ethylenically unsaturated group selected from the group consisting of



$CX_2= CX-E-$, and

$CX_2= CX-CH_2-E-$,

wherein E = O or S;

each X is individually H, D, F, or Cl;

n is 1 if R is divalent, and 2 if R is trivalent;

and n' is 1 if R' is divalent and 2 if R' is trivalent.

16. The composition of claim 14 wherein the connecting groups R and R' are individually selected from the group consisting of $-CH_2-$ and $-CH_2CHCH_2OCH_2-$.

17. The energy curable composition of claim 1 wherein the at least difunctional thiol compound includes a perfluorinated moiety.

18. The energy curable composition of claim 17 wherein the at least difunctional thiol compound has the structure

$(HS)_n-R-R_f-R'-(SH)_n$,

wherein

R_f is a perfluorinated moiety selected from the group consisting of:

$-(CF_2)_x-$,

$-(C_6F_4)_x-$,

$-(CF_3)_2C-$,

$-CF_2O-[(CF_2CF_2O)_m(CF_2O)_n]-CF_2-$,

$-CF(CF_3)O(CF_2)_4O[CF(CF_3)CF_2O]_pCF(CF_3)-$, and

$-CF_2O-(CF_2CF_2O)_m-CF_2-$,

wherein x is an integer between 1 and about 10;

m and n designate the number of randomly distributed perfluoroethyleneoxy and perfluoromethyleneoxy backbone repeating subunits, respectively; and

p designates the number of $-\text{CF}(\text{CF}_3)\text{CF}_2\text{O}-$ backbone repeating subunits;

R and R' are divalent or trivalent connecting moieties selected individually from the group consisting of alkyl, aryl, ester, ether, amide, amine, and urethane groups;

n is 1 if R is divalent, and 2 if R is trivalent; and

n' is 1 if R' is divalent and 2 if R' is trivalent.

19. The energy curable composition of claim 18 wherein the divalent or trivalent connecting moieties R and R' are selected individually from the group consisting of

$-\text{CH}_2\text{O}_2\text{CCH}_2\text{CH}_2-$,

$-\text{CH}_2-$, and

$-\text{CH}_2\text{CHCH}_2\text{OCH}_2-$.

20. A polymeric material comprising:

thioether moieties in a concentration of at least about 0.05 M; and
at least one perhalogenated moiety.

21. The polymeric material of claim 20 further comprising a C_H of less than about 55 M.

22. The polymeric material of claim 20 wherein the perfluorinated moiety is selected from the group consisting of

$-(\text{CF}_2)_x-$,

$-(\text{C}_6\text{F}_4)_x-$,

$-(\text{CF}_3)_2\text{C}-$,

$-\text{CF}_2\text{O}-[(\text{CF}_2\text{CF}_2\text{O})_m(\text{CF}_2\text{O})_n]-\text{CF}_2-$,

$-\text{CF}(\text{CF}_3)\text{O}(\text{CF}_2)_4\text{O}[\text{CF}(\text{CF}_3)\text{CF}_2\text{O}]_p\text{CF}(\text{CF}_3)-$, and

$-\text{CF}_2\text{O}-(\text{CF}_2\text{CF}_2\text{O})_m-\text{CF}_2-$,

wherein x is an integer between 1 and about 10;
 m and n designate the number of randomly distributed perfluoroethyleneoxy and
 perfluoromethyleneoxy backbone repeating subunits, respectively; and
 p designates the number of $-\text{CF}(\text{CF}_3)\text{CF}_2\text{O}-$ backbone repeating subunits.

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23. An optical element comprising a polymeric core including a polymeric material
 including thioether moieties in a concentration of at least 0.05 M and at least one at least
partially halogenated moiety.

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24. The optical element of claim 23 further comprising:

- a polymeric overclad layer;
- a polymeric cladding layer; and
- a substrate

wherein the polymeric core is contiguous on at least one side with polymeric overclad
 layer, and contiguous on at least one side with the polymeric cladding layer; and the
 polymeric cladding layer is between the polymeric core and the substrate.

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25. The optical element of claim 23 wherein the perfluorinated moiety is selected from the
 group consisting of

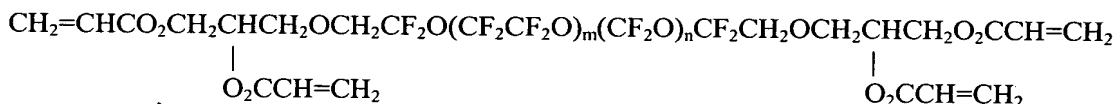
- $-(\text{CF}_2)_x-$,
- $-(\text{C}_6\text{F}_4)_x-$,
- $-(\text{CF}_3)_2\text{C}-$,
- $-\text{CF}_2\text{O}-[(\text{CF}_2\text{CF}_2\text{O})_m(\text{CF}_2\text{O})_n]-\text{CF}_2-$,
- $-\text{CF}(\text{CF}_3)\text{O}(\text{CF}_2)_4\text{O}[\text{CF}(\text{CF}_3)\text{CF}_2\text{O}]_p\text{CF}(\text{CF}_3)-$, and
- $-\text{CF}_2\text{O}-(\text{CF}_2\text{CF}_2\text{O})_m-\text{CF}_2-$,

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wherein x is an integer between 1 and about 10;
 m and n designate the number of randomly distributed perfluoroethyleneoxy and
 perfluoromethyleneoxy backbone repeating subunits, respectively; and
 p designates the number of $-\text{CF}(\text{CF}_3)\text{CF}_2\text{O}-$ backbone repeating subunits.

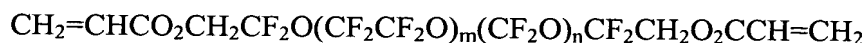
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26. The optical element of claim 23 wherein the polymeric material is produced from a energy curable composition including the compound



wherein m and n designate the number of randomly distributed perfluoroethyleneoxy and perfluoromethyleneoxy backbone repeating subunits, respectively, and the ratio of m:n is between about 0.5:1 and about 1.4:1.

27. The optical element of claim 23 wherein the polymeric material is produced from an energy curable composition including the compound



wherein m and n designate the number of randomly distributed perfluoroethyleneoxy and perfluoromethyleneoxy backbone repeating subunits, respectively, and the ratio of m:n is between about 0.5:1 and about 1.4:1.

28. The optical element of claim 23 wherein the optical loss of the polymeric core is less than 0.75 dB/cm at 1550 nm and less than 0.75 dB/cm at 1617 nm.

29. The optical element of claim 23 wherein the optical loss of polymeric core is less than 0.5 dB/cm at 1550 nm and less than 0.5 dB/cm at 1617 nm.

30. The optical element of claim 24 wherein the glass transition temperature of the polymeric overclad layer and the polymeric clad layer is about 40 °C or less and the glass transition temperature of the polymeric core is about 50 °C or less.

31. The optical element of claim 24 wherein the glass transition temperature of the polymeric core is less than 0 °C.

32. The optical element of claim 24 wherein the polymeric overclad layer and the polymeric clad layer include a polymeric material including thioether moieties in a concentration of at least 0.05 M and at least one at least partially halogenated moiety.

33. A method of making an optical element comprising the steps of:

(a) applying a layer of a clad composition to a substrate, the clad composition including an at least difunctional thiol compound, an at least difunctional ethylenically unsaturated compound, and a selected amount of a free radical initiator

wherein at least one of the thiol compound and the ethylenically unsaturated compound is at least partially halogenated,
the ratio of thiol moieties to isolated ethylenically unsaturated moieties is between about 1:2 and about 2:1 and
the ethylenically unsaturated compound account for between about 35% and about 99.9% of the cladding composition;

(b) at least partially curing the cladding composition to form a polymeric cladding layer;

(c) applying a photosensitive core composition to the surface of the polymeric cladding layer to form a core composition layer, the core composition including an at least difunctional thiol compound, an at least difunctional ethylenically unsaturated compound, and a selected amount of a free radical initiator

wherein at least one of the thiol compound and the ethylenically unsaturated compound is at least partially halogenated,
the ratio of thiol moieties to isolated ethylenically unsaturated moieties is between about 1:2 and about 2:1 and
the ethylenically unsaturated compound accounts for between about 35% and about 99.9% of the core composition;

(d) imagewise exposing the photosensitive core composition layer to sufficient actinic radiation to effect the at least partial polymerization of an imaged

portion and to form at least one non-imaged portion of the photosensitive core composition layer;

(e) removing the at least one non-imaged portion without removing the imaged portion, thereby forming a polymeric patterned core from the imaged portion;

(f) applying a photosensitive overlaid composition onto the polymeric patterned core; and

(g) at least partially curing the overlaid composition to form a polymeric overlaid layer,

wherein the polymeric overlaid layer and the polymeric cladding layer have a lower refractive index than the polymeric patterned core.

34. The method of claim 33 wherein the overlaid composition includes an at least difunctional thiol compound, an at least difunctional ethylenically unsaturated compound, and a selected amount of a free radical initiator wherein at least one of the thiol compound and the ethylenically unsaturated compound is at least partially halogenated, the ratio of thiol moieties to isolated ethylenically unsaturated moieties is between about 1:2 and about 2:1 and the ethylenically unsaturated compound account for between about 35% and about 99.9% of the overlaid composition.